High Performance of Iron(III) Phosphate for Selective Oxidation of Methanol

Dimitar Klissurski,[a] Vicente Rives,*[b] Nevena Abadzhjieva,[a] Yordanka Pesheva,[a] Philip Pomonis,[c] T. Sdoukos[c] and Dimitris Petrakis[c]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[b] *Departamento de Química Inorgánica, Universidad de Salamanca, Facultad de Farmacia, 37007-Salamanca, Spain*
[c] *Department of Chemistry, University of Ioannina, Ioannina, Greece*

A high selectivity of iron(III) phosphate-based catalysts in the oxidation of methanol to formaldehyde has been established and explained on the basis of the high covalency of the P–O bonds.

It has been shown in previous studies[1] that the activity and selectivity of metal oxides in the catalytic decomposition or oxidation of aliphatic alcohols depend on the ionic character of the metal–oxygen bond. Conversely, the adsorptive properties of oxysalts could be related to the ionic character of the bonds within the ionic group, *i.e.*, between oxygen and the third component of the double oxide system.[2] In this context, a comparison between iron(III) molybdate, widely used for selective heterogeneous catalytic oxidation, and iron(III) phosphate, could be of interest. The relative electronegativities of P^{5+} and Mo^{6+} ions are[2] 67.9 and 66.6, respectively, and the ionicity I of the X–O bonds (X = P^{5+} or Mo^{6+}) are 27.5 and 28.9%, respectively. Obviously, both parameters have very close values. In view of this, it could be expected that a similarity in the catalytic behaviour of iron(III) molybdate, which is known as a highly selective catalyst for methanol oxidation to formaldehyde, and iron(III) phosphate, should exist theoretically. Since the X–O bond in iron(III) phosphate is to some extent more covalent than in the molybdate, its oxygen should exhibit a lower reactivity and a larger selectivity in methanol mild oxidation would be expected.

Catalysts based on iron(III) phosphate were prepared by calcination of $FePO_4 \cdot 4H_2O$ (Fluka, p.a.) for 5 h in air at 773 K. Its specific surface area, as determined by the Brunauer–Emmett–Teller method, was 4.9 m² g⁻¹. A Möss-

bauer characterisation of the catalyst specimen was performed in the constant acceleration mode. The isomer shifts (δ) were determined with respect to the centre of gravity of the spectrum of α-Fe. The spectra were processed by the least squares method, assuming Lorentz-shaped lines. The main kinetic parameters of methanol oxidation were investigated using a flow apparatus.[3] The flow rate of the methanol–air reaction mixture was 4 cm³ s⁻¹ at a methanol concentration of 4.0% vol. The formaldehyde content in the reaction products has been determined by the hydrogen sulfite method, and CO and CO_2 were analysed by gas chromatography.[4]

The temperature dependence of the degrees of conversion of methanol to formaldehyde, CO_x and selectivity is shown in Fig. 1. As can be seen, oxidation of methanol to formaldehyde on the precalcined $FePO_4 \cdot 4H_2O$ proceeds with an extremely high selectivity (close to 100% in the temperature range 570–650 K). The activation energy of the reaction was found to be 56.6 kJ mol⁻¹. This value is close to those obtained for the typical selective catalysts used for partial oxidation of methanol.[5] Oxidation of methanol to CO_2 takes place at temperatures higher than 650 K. However, the rate of this secondary reaction still remains very low, which determines the high selectivity of iron(III) phosphate-based catalysts towards methanol oxidation to formaldehyde at relatively high temperatures (up to 720 K).
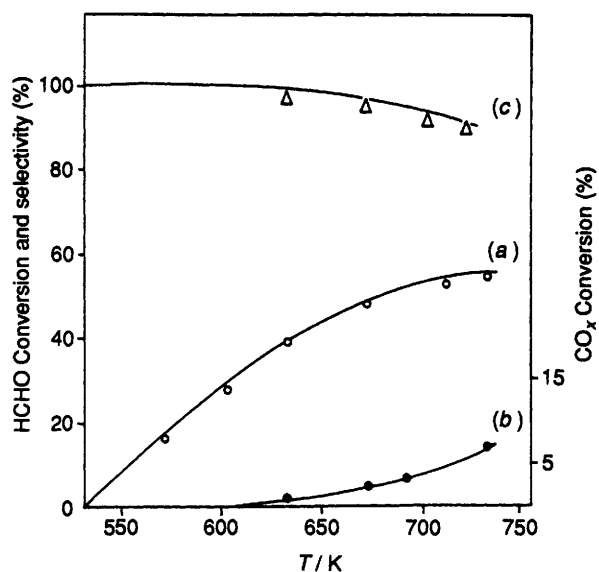
Fig. 1 Conversion of methanol on iron(III) phosphate catalyst: (a) CH_3OH conversion to HCHO; (b) CH_3OH conversion to CO_x; (c) HCHO selectivity

Preliminary information concerning the stationary state of the catalyst has been obtained by Mössbauer spectroscopy, which is a particularly suitable technique for characterization of the oxidation state of iron, as well as of the catalyst phase composition.

The Mössbauer spectrum of the precalcined, untested catalyst can be considered as a superposition of two doublets with different values of the main parameters: isomeric shifts (δ_1, δ_2), quadrupole splitting (Δ_1, Δ_2) and linewidths (Γ_1, Γ_2), Table 1. This can be considered as indicative of the existence of, at least, two phases. The first doublet has parameter values close to those of dehydrated $FePO_4 \cdot 4H_2O$ reported by Millet et al.[6] The second doublet has a considerably higher value of quadrupole splitting $(\Delta_2 = 1.14)$. Its parameters are similar, but not completely identical, to those of Fe_3PO_7.[7,8]

After the catalytic tests, a rather complex spectrum is observed. It includes lines of four doublets, two of them corresponding to $FePO_4$ and presumably to Fe_3PO_7. The identification of the second new phase has been difficult, due to the low intensities of all the lines, and it can be tentatively assumed to be $Fe_2P_2O_7$. In addition to this phase composition, a small amount of Fe_2O_3 (ca. 2–3% m/m) is also formed.

A more precise assignment of the observed spectra to definite phases needs some further Mössbauer and X-ray diffraction studies, which are now in progress.[9] It is obvious, however, that the phase composition of the catalysts in a stationary state is significantly different from the initial one.

Table 1 Calculated Mössbauer parameters of iron(III) phosphate[a]

Initial	Calcined		Used catalyst			
$\delta\,0.41$	$\delta_1\,0.34$	$\delta_2\,0.35$	$\delta_1\,0.32$	$\delta_2\,0.36$	$\delta_3\,1.43$	$\delta_4\,1.24$
$\Delta\,0.68$	$\Delta_1\,0.66$	$\Delta_2\,1.26$	$\Delta_1\,0.52$	$\Delta_2\,1.14$	$\Delta_3\,2.18$	$\Delta_4\,2.05$
$\Gamma\,0.44$	$\Gamma_1\,0.31$	$\Gamma_2\,0.46$	$\Gamma_1\,0.45$	$\Gamma_2\,0.55$	$\Gamma_3\,0.25$	$\Gamma_4\,0.25$
$G\,100$	$G_1\,62$	$G_2\,38$	$G_1\,45$	$G_2\,53$	$G_3\,1$	$G_4\,1$

[a] δ Isomeric shift/mm s^{-1}; Δ quadrupole splitting/mm s^{-1}; Γ line width/mm s^{-1}; G relative mass (%) of component i.

It is important to note that the main Mössbauer parameters of the new phases formed during the catalytic reaction (isomeric shifts δ_3 1.43 and δ_4 1.24 mm s^{-1}, and quadrupole splitting values of Δ_3 2.18 and Δ_4 2.05) indicate the presence of Fe^{2+}, i.e., they show that the catalysts undergo a partial reduction during the catalytic tests.

A similar catalyst modification has been observed in our previous studies on the methanol oxidation over Fe^{3+} and $Fe^{3+}-Cr^{3+}$ molybdate based catalysts.[5] Formation of a surface layer of iron(III) oxide during calcination can be excluded because Fe_2O_3 is not selective for the mild oxidation of MeOH to HCHO.[1,2]

The results of the present study show that, in agreement with some theoretical concepts,[1,2] iron(III) phosphate-based catalysts exhibit a high selectivity towards methanol partial oxidation to formaldehyde, and could have not only theoretical, but also a practical interest.

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